

Evidence for the Transition between Concerted and Stepwise Heterogeneous Electron Transfer–Bond Fragmentation Mechanisms

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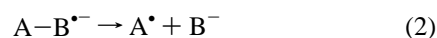
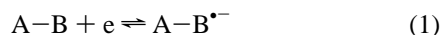
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Abstract: The electrochemical reduction of *tert*-butyl *p*-cyanoperbenzoate in DMF leads to the cleavage of the oxygen–oxygen bond. A subsequent reaction yielding *tert*-butyl *p*-cyanobenzoate could be avoided by the addition of a mild acid, with the result that the main reduction peak was affected only by the kinetics of the electron transfer bond fragmentation process. Unusual features of the heterogeneous electron transfer mechanism were evidenced by the conventional voltammetric criteria, which pointed to a nonlinear potential dependence of the transfer coefficient α . The fine details of the electron transfer mechanism were obtained by convolution analysis of the voltammetric curves, a procedure that led to a bell-shaped potential dependence of α . The observed behavior is explained by the assumption that when the electrode potential is decreased, the process changes from a concerted electron transfer bond cleavage to a partially stepwise mechanism. The observed potential dependence of α is in agreement with the results from simple calculations aimed to obtain the potential dependences of α expected for the two pure mechanisms.

Introduction

A relevant amount of recent studies has been devoted to the study of thermally-induced¹ or photoinitiated² electron transfer (ET) processes that are associated with bond fragmentation. It is now reasonably well established that the mechanism by which an acceptor molecule (AB) is dissociatively reduced to form a radical (A[•]) and an anion (B[−]) can be either stepwise (eqs 1 and 2) or concerted (eq 3).³ The fact that one mechanism may



prevail over the other depends on several factors. The difference in the reaction free energy (ΔG°) between ET 1 and ET 3 is given by the difference between the corresponding standard potentials $E^{\circ}_{AB/AB^{\bullet-}}$ and $E^{\circ}_{AB/A^{\bullet}B^{-}}$. Since the latter potential can be expressed, thanks to a thermochemical cycle,⁴ through eq 4, it follows that when the A–B bond dissociation free energy

$$E^{\circ}_{AB/A^{\bullet}B^{-}} = E^{\circ}_{B^{\bullet}/B^{-}} - \text{BDFE}/F \quad (4)$$

(BDFE) is small and/or $E^{\circ}_{B^{\bullet}/B^{-}}$ is positive enough, the chances for a dissociative ET to provide the preferred reaction path are enhanced. This is, however, a necessary but not sufficient condition because even if $E^{\circ}_{AB/AB^{\bullet-}}$ is significantly more

negative than $E^{\circ}_{AB/A^{\bullet}B^{-}}$, the activation free energies of the two processes [$(\Delta G^{\ddagger})_1$ and $(\Delta G^{\ddagger})_3$] may provide the actual discriminating factor. According to the current theories of outersphere ET⁵ and dissociative ET,³ the ET 1 ($n = 1$) and ET 3 ($n = 3$) can be expressed by a formally identical activation–driving force relationship (eq 5), the only difference being the nature of the intrinsic barrier (ΔG_0^{\ddagger}), i.e., the activation free energy at zero driving force. In fact, $(\Delta G_0^{\ddagger})_1$ and $(\Delta G_0^{\ddagger})_3$ are given by

$$(\Delta G^{\ddagger})_n = (\Delta G_0^{\ddagger})_n \left[1 + \frac{(\Delta G^{\circ})_n}{4(\Delta G_0^{\ddagger})_n} \right]^2 \quad (5)$$

$\lambda/4$ and $(\lambda + \text{BDE})/4$, respectively, where λ is the sum of the internal and the solvent reorganization energies and BDE is the bond dissociation energy.^{3,5} From a practical point of view, this leads to a quite relevant difference, because if we consider typical dissociative-type systems such as halides^{1a,3} and peroxides,^{4,6,7} the contribution of the BDE term to the intrinsic barrier amounts to 70–80%. As a consequence, ET 1 and ET 3 respond to changes in the reaction free energy in a very different way and this may result in a smaller $(\Delta G^{\ddagger})_1$ relative to $(\Delta G^{\ddagger})_3$, in spite of a less favorable reaction free energy for ET 1 than for ET 3.⁸

The adiabatic dissociative ET theory has been proposed by Savéant only a few years ago,⁹ and although different experimental systems have provided positive feedback, further tests

(5) For example, see: Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265.

(6) Workentin, M. S.; Maran, F.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 2120.

(7) Maran, F.; Wayner, D. D. M.; Workentin, M. S.; *et al.* Manuscript in preparation.

(8) Differences may arise also because of different preexponential terms in the rate expression for ET 1 and ET 3. Although the formation of the radical anion is likely an essentially adiabatic ET process, there are reasons to believe that the concerted ET to peroxides can be nonadiabatic.^{6,7} This would result in a smaller preexponential factor for ET 3 and thus, at a given potential, to a less relevant weight of the rate of ET 3 relative to that of ET 1.

(9) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

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(2) (a) Saeva, F. D. In *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1990; Vol. 156, p 59. (b) Schuster, G. B. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 163. (c) Maslak, P. In *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1993; Vol. 168, p 1. (d) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292.

(3) Savéant, J.-M. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 4, p 53.

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are still necessary to better define its scope and limitations. In general, a very good way to test the dissociative ET theory is to find well-behaved experimental systems in which the transition between a stepwise and a concerted mechanism can be observed. In this context and as can be argued on the basis of the above discussion, the energy of the donor and thus the free energy of the reactant system is quite important, independent of the fact that one deals with a solution ET or a heterogeneous ET. When the standard potential for the formation of the electron donor (homogeneous ET) or the electrode potential E is changed to more positive values, it may be possible, in principle, to obtain a transition from a stepwise to a concerted mechanism. As described above, such a transition is expected to be mainly⁸ due to the different ways by which $(\Delta G^\ddagger)_1$ and $(\Delta G^\ddagger)_3$ respond to free energy changes. In the borderline situation, the system is in an energy range in which the acceptor molecule AB can be reduced through both mechanisms, although with different rates.

The C–S bond cleavage induced upon ET to triphenylmethyl phenyl sulfide by a series of aromatic electron donors provides the only experimental observation of such a transition under homogeneous conditions.¹⁰ When the reaction free energy was varied by 0.5 eV, it was in fact possible to observe the predicted,¹¹ S-shaped activation–driving force relationship. However, the homogeneous approach is intrinsically less sensitive than the corresponding heterogeneous one. Whereas in the heterogeneous case the reorganization energy λ depends essentially only on the acceptor molecule, the homogeneous λ and, therefore, the intrinsic barrier $(\Delta G_0^\ddagger)_h$ depend also on the dimension and the structure of the one-electron donor. Moreover, and quite important for practical reasons, whereas in the homogeneous case the number of electron donors is forcefully limited, in the heterogeneous approach the free energy of the reaction can be varied continuously by simply changing the applied potential E ; as a result, the quantity of data that can be collected is significantly larger, with obvious consequences in terms of precision and reliability of the data. Indeed, voltammetric effects coherent with a transition behavior have been recently reported for the reduction of two sulfonium cations;¹² however, since the conventional voltammetric analysis¹³ was applied, only an approximate, though indicative, picture of the ET mechanism could be obtained. In terms of sensitivity to ET rate changes, an initial problem associated with the conventional voltammetric approach is that although an irreversible peak such as those observed for mechanisms 1 and 2 or mechanism 3 develops over a potential range of some hundred millivolts, only two points of the voltammetric curve are actually analyzed, i.e., those corresponding to the peak potential (E_p) and the potential at mid-peak height ($E_{p/2}$). A second drawback is that if one uses the conventional voltammetric equations, a linear activation–driving force relationship is implicitly assumed;¹³ therefore, the results are forcefully approximated if a rate law such as that given in eq 5 is better at describing the actual experimental system.

The convolution analysis of the voltammetric curves provides a powerful tool to study fine details of electrode processes. Although this method has been presented many years ago,¹⁴ it

has not been used often for kinetic purposes in recent years, with the result of being very little known. This method, however, is very precise, and we believe it to be particularly useful in the study of ET reaction associated with fast bond cleavage reactions. It should be emphasized that, unlike the conventional voltammetric approach, *all* of the data points composing the voltammetric curve are used in the kinetic analysis and, moreover, that *no a priori assumption* on the ET rate law has to be assumed in the analysis of the experimental data. Very recently, we applied this experimental approach to the study of the dissociative ET to a series of dialkyl peroxides, and by analysis of the irreversible voltammetric peaks, we were able to obtain thermodynamic results, such as the E_{AB/A^+B^-} values and the corresponding BDFEs, in good agreement with available thermochemical information.⁴ With such a support, we were therefore confident that, since it is possible to collect a considerable amount of rate-driving force data through convolution of (good) experimental voltammetric curves, this method would have provided a very good choice in detecting possible changes in the ET mechanism.

In this paper, the results we obtained on the electrochemical reduction of *tert*-butyl *p*-cyanoperbenzoate (CP) in DMF, in comparison with those of the corresponding ester, *tert*-butyl *p*-cyanobenzoate (CB), are described. The reduction was studied by cyclic voltammetry followed by convolution analysis of the data. Due to the particular experimental system selected and the quality of the data, we obtained evidence for a well-behaved case of a borderline ET bond fragmentation mechanism. This is in good agreement with what is expected on the basis of the above discussion and therefore in line with the concepts and consequences underlying the dissociative ET theory.

Experimental Section

Chemicals. *N,N*-Dimethylformamide (Janssen, 99%) and tetrabutylammonium perchlorate (TBAP, 99%, Fluka) were purified as previously described.⁴ *tert*-Butyl *p*-cyanoperbenzoate¹⁵ was prepared from *tert*-butyl hydroperoxide and *p*-cyanobenzoyl chloride: ¹H NMR (200 MHz, CDCl₃, TMS) δ 1.42 (9H, s, *t*-Bu), 7.7–8.1 (4H, AA'BB', C₆H₄). *tert*-Butyl *p*-cyanobenzoate¹⁶ was prepared from *tert*-butyl alcohol and *p*-cyanobenzoyl chloride. *p*-Cyanobenzoic acid (Aldrich, 99%) and tetrabutylammonium hydroxide 30-Hydrate (Fluka, 99%) were used as received.

Electrochemical Apparatus and Procedures. The glassy carbon electrode was built from a glassy carbon rod (Tokai GC-20), treated, and stored as previously described.⁴ Before each measurement, the electrode was polished with a 0.25 μ m diamond paste (Struers), ultrasonically rinsed with ethanol for 5 min, and electrochemically activated in the background solution by means of several cycles at 0.5 V s⁻¹ between 0 and -2.8 V against the KCl saturated calomel electrode (SCE). The reference electrode was a homemade Ag/AgCl, its potential being calibrated after each experiment against the ferrocene/ferricinium couple (in DMF/0.1 M TBAP, $E_{Fc/Fc^+} = 0.464$ V vs SCE). In the following, all of the potential values will be reported against SCE. The counterelectrode was a 1 cm² Pt plate. The electrochemical instrumentation employed for cyclic voltammetry was the same as recently described.⁴ The feedback correction was applied to minimize the ohmic drop between the working and reference electrodes. The confidence in the positive feedback was judged as already described, i.e., by checking the voltammetric behavior of a couple of known ET kinetics;⁴ in addition, the agreement between the different sets of kinetic data provided an a posteriori test of it, as described in the Results and Discussion.

Electrochemical measurements were conducted in an all glass cell, thermostated at 25 \pm 0.2 °C. The solution was carefully deoxygenated

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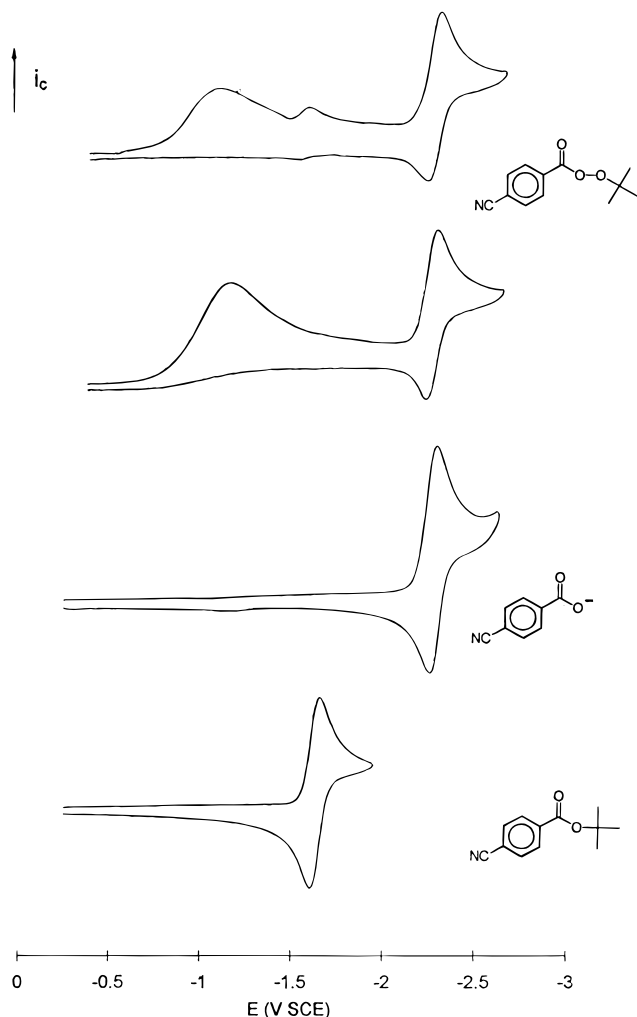


Figure 1. Cyclic voltammograms for the reduction of (top to bottom) CP, CP in the presence of an equivalent amount of acetanilide, *p*-cyanobenzoic acid in the presence of an equivalent amount of tetrabutylammonium hydroxide, and CB. The curves were obtained in DMF/0.1 M TBAP at the glassy carbon electrode; $T = 25\text{ }^{\circ}\text{C}$.

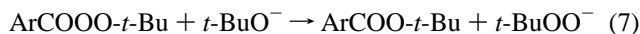
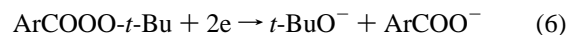
with Argon (SIAD, 99.9995%), and a blanket of gas was then maintained over the liquid. For quantitative measurements, the behavior of the glassy carbon electrode was first studied in the background solution, in a selected potential range and for scan rates ranging from 0.1 to 200 V s^{-1} . The cyclic voltammograms were recorded by the digital oscilloscope, using the necessary expedients to reduce the electrical noise,⁴ and then transferred to a PC. The substrate was then added to the solution, and the same procedure was repeated. The corresponding background curves were subtracted from the cyclic voltammograms to eliminate the contribution of the capacitive current. The resulting curves were then analyzed by the conventional voltammetric criteria¹³ and the convolution approach,^{14,17} using specially designed laboratory software. Digital simulations of some of the cyclic voltammetry curves were performed by using the DigiSim 2.0 software by Bioanalytical Systems Inc.

Results and Discussion

The voltammetric reduction of CP in DMF/0.1 M TBAP gives rise to three reduction peaks (Figure 1). The main reduction peak is irreversible, and its peak potential is -1.21 V when the scan rate (ν) is 0.2 V s^{-1} . The second peak, $E_p = -1.63\text{ V}$, is detectable only at low ν and is due to the reversible reduction of CB, as verified by comparison with the cyclic voltammetry of an authentic sample of it. The third reduction peak at -2.30 V is reversible and corresponds to the reduction of the

carboxylate ArCOO^- ; the same anion is also responsible for an irreversible oxidation peak at 1.56 V that can be detected in the positive-going scan after reduction of CP. Information on both the reductive and oxidative behavior of ArCOO^- was obtained by studying the electrochemical behavior of an authentic sample of the carboxylate, obtained *in situ* by reaction of *p*-cyanobenzoic acid with tetrabutylammonium hydroxide.

In analogy with the behavior that we are observing with other perbenzoates,¹⁸ the reduction of CP leads to the cleavage of the O–O bond, according to the overall reaction in eq 6. The leaving group B^- in eqs 2 and 3 is easily identified as ArCOO^- , which better accommodates the negative charge; on the other hand, eq 6 takes into account that, at the potentials of the peak, the reduction of the radical fragment $t\text{-BuO}^\bullet$ ($E^\circ = -0.23\text{ V}$)⁶ also occurs. The electrogeneration of the anion $t\text{-BuO}^-$ causes



the formation of the ester CB through substitution (eq 7). The latter reaction is very sensitive to the presence of water traces, since $t\text{-BuOH}$ ($\text{p}K_a = 32.5$) is less acidic than H_2O by 0.8 $\text{p}K_a$ unit;¹⁹ accordingly, the height of the CB peak and, therefore, the amount of CP which is formed are a function of the concentration of the still-surviving $t\text{-BuO}^-$ anion.²⁰ The decay of CP by chemical means, however, can be efficiently hampered by protonation of $t\text{-BuO}^-$ with a weak, nonreducible acid such as acetanilide ($\text{p}K_a = 22.3$).^{19b} As a result, the reduction of CP gives rise to a two-electron peak (eq 6), the potential of the first peak is slightly more negative (-1.26 V), and the peak of CB disappears (see Figure 1). This overall behavior is coherent with what expected when the starting material undergoes a reaction with an electrogenerated intermediate (parent–child reaction).²¹ Since the focus of the present work was to obtain the rate law by which the uptake of the first electron takes place, all of the data described below were collected in the presence of acetanilide, to ensure a constant electron consumption in the overall time scale required by the voltammetry experiments.

The conventional voltammetric analysis of the reduction peak of CP revealed anomalous features (Figures 2 and 3). When ν was increased, the absolute slope of the E_p vs $\log \nu$ plot was found to decrease in the $0.1\text{--}20\text{ V s}^{-1}$ range and then increase for higher ν values (Figure 2). The peak width, $\Delta E_{p/2}$, i.e., the difference between $E_{p/2}$ and E_p , decreases upon increasing ν , reaches the minimum value of 150 mV at 20 V s^{-1} , and then increases for higher scan rates (Figure 2). Figure 3 shows a typical series of the ν -normalized voltammograms where it can be seen that $i_p/\nu^{1/2}$ initially increases with ν , reaches a maximum at $10\text{--}20\text{ V s}^{-1}$, and decreases thereafter. Such an overall behavior not only indicates that the transfer coefficient α is ν -dependent, as found with other peroxides,^{4,18} but also and most important that such a dependence is far from being linear. For example, the average value of the apparent transfer coefficient

(18) Antonello, S.; Maran, F.; *et al.* Work in progress.

(19) The $\text{p}K_a(\text{DMF})$ of $t\text{-BuOH}$ and that of water can be obtained from the corresponding DMSO data^{19a} using the correlation $\text{p}K_a(\text{DMF}) = 1.56 + 0.96 \text{p}K_a(\text{DMSO})$.^{19b} (a) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295. (b) Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320.

(20) When $t\text{-BuO}^-$ is protonated, the so-formed OH^- is liable to attack CP with formation of the corresponding acid, whose main action is to act as a proton donor.

(21) For example, see: Maran, F.; Roffia, S.; Severin, M. G.; Vianello, E. *Electrochim. Acta* **1990**, *35*, 81.

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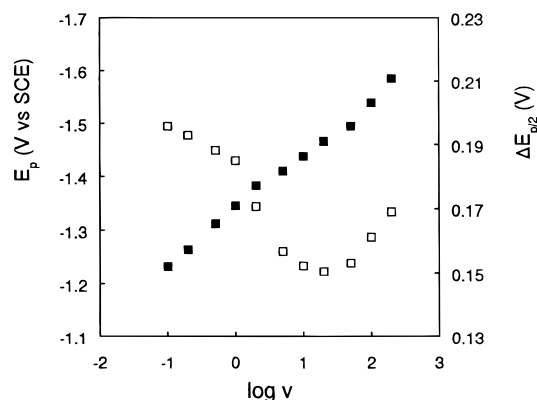


Figure 2. Scan rate dependence of the voltammetric peak potential (■) and peak width (□) for the reduction of 1.47 mM CP in DMF/0.1 M TBAP at the glassy carbon electrode. The measurements were carried out at 25 °C in the presence of an equivalent amount of acetanilide.

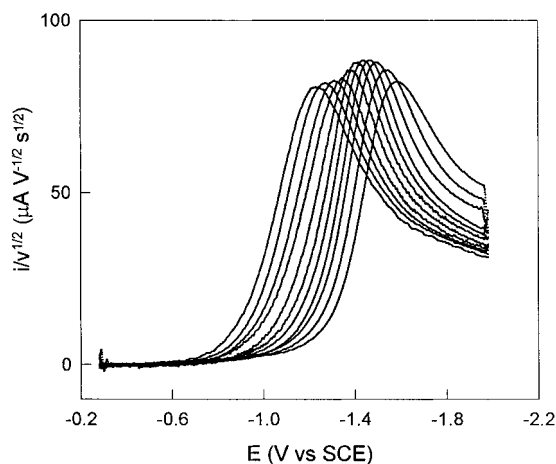


Figure 3. Background-subtracted linear scan voltammograms for the reduction of 1.47 mM CP in DMF/0.1 M TBAP at the glassy carbon electrode. For the sake of comparison, the faradaic current is reported in the usual v -normalized form. The scan rates were (left to right): 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200 $V s^{-1}$. $T = 25$ °C.

α_{app} (i.e., double-layer uncorrected)²² that can be calculated²³ from $\partial E_p/\partial \log v$ is 0.26 at $v < 2 V s^{-1}$, 0.35 at $2 \leq v \leq 20 V s^{-1}$, and 0.20 at $v > 20 V s^{-1}$; similarly, the average α_{app} values calculated from the $\Delta E_{p/2}$ ²³ are 0.25, 0.28, 0.32, and 0.28 at 0.2, 2, 20, and 200 $V s^{-1}$, respectively.²⁴

As recently shown for the reduction of dialkyl peroxides,⁴ the convolution analysis of the voltammetric data provides a more powerful way than the direct voltammetric analysis to observe the details of the electrode process. Accordingly, the background-subtracted voltammograms, obtained at nine different scan rates in the 0.1–50 $V s^{-1}$ range and digitalized 1

(22) The difference between α and α_{app} is given by the equation^{4,22a} $\alpha = \alpha_{app}/(1 - \partial\phi^{\#}/\partial E)$, where $\phi^{\#}(E)$ is the difference between the potential at the average distance at which the substrate is located when the electron transfer takes place and the potential of the bulk solution. For mercury, for example, in the same solvent/electrolyte and potential range and under the usual hypothesis that the reaction site can be identified with the outer Helmholtz plane,^{13c,22b} α_{app} is systematically smaller than α by only 3%.^{22c} (a) Savéant J.-M.; Tessier, D. *Faraday Discuss. Chem. Soc.* **1982**, 74, 57. (b) Severin, M. G.; Arévalo, M. C.; Maran, F.; Vianello, E. *J. Phys. Chem.* **1993**, 97, 150. (c) Arévalo, M. C.; Rodríguez, J. L.; Severin, M. G.; Vianello, E. Unpublished results.

(23) α_{app} can be calculated from the equations $|\partial E_p/\partial \log v| = 1.15RT/F\alpha_{app}$ and $\Delta E_{p/2} = 1.857RT/F\alpha_{app}$.¹³

(24) When the cyclic voltammograms are simulated, assuming that a linear activation-driving force relationship holds in the potential range spanned by each peak up to E_p and by using the α values obtained from the experimental $\Delta E_{p/2}$ values, it is possible to obtain an $i_p/v^{1/2}$ vs $\log v$ pattern that matches the experimental values pretty well, the average difference being 2% in the 0.1–100 $V s^{-1}$ range.

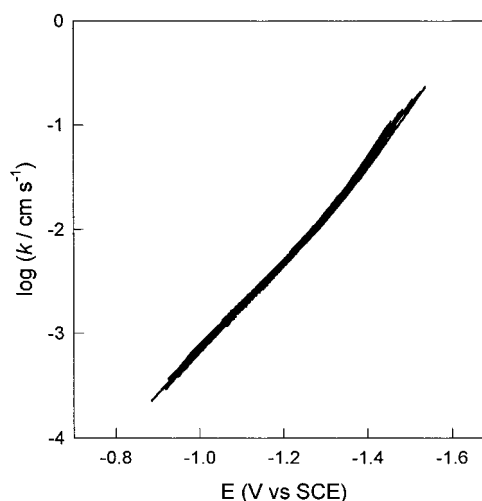


Figure 4. Potential dependence of the logarithm of the heterogeneous rate constant for the reduction of CP in DMF/0.1 M TBAP at 25 °C. The plot is formed from a collection of curves obtained in four separate experiments.

point/mV, were subjected to the convolution procedure followed by logarithmic analysis, using the equation which holds for an irreversible process.²⁵ The corresponding $\log k(E) - E$ plots are shown in Figure 4. For each scan rate and four separate experiments carried out with different samples of CP, the logarithmic analysis led to the potential dependence of the heterogeneous rate constant $k(E)$ in a range of 0.35–0.40 V. Taking into account that when v is increased, the peak shifts toward more negative potentials, it should be stressed that in this way 12–36 $k(E)$ determinations per millivolt were eventually carried out in the –1.0 to –1.5 V range. Two main features can be noticed in the figure, namely, the satisfactory agreement between the different sets of data (the average standard deviation is 7%) and an unusual but definite upward curvature in a potential range from ca. –1.1 to –1.4 V in the overall plot.²⁶

Each logarithmic plot was treated separately to obtain the corresponding derivative plot, which is linked to α_{app} through eq 8. The experimental α_{app} values were obtained by linear

$$\alpha_{app} = -\frac{RT}{F} \left(\frac{d \ln k}{dE} \right) \quad (8)$$

regression of the $\ln k(E)$ data within 20–30 mV E intervals. Since the only inert electrode for the reduction of perbenzoates is glassy carbon,¹⁸ the double-layer properties of which are yet unknown, the α_{app} data could not be corrected for the double layer. However, we have previously observed that in the explored E range even uncorrected transfer coefficient data provide a reasonable representation of the process,^{4,22} and accordingly, we assume in the following that $\alpha \approx \alpha_{app}$.

To exemplify the results of such a procedure, Figure 5 shows both the voltammetric curve and the α analysis obtained in one of the experiments for scan rates of 0.2 and 20 $V s^{-1}$. Both graphs provide an example of the remarkably good agreement we found between each set of convolution α data and the α

(25) The equation is¹⁷ $\ln k = \ln D^{1/2} - \ln[(I_1 - I(t))/i(t)]$, where real (i) and convoluted (I) current values are combined; a limiting convolution current (I_1) is reached when the electrode process becomes diffusion controlled.¹⁴ For CP, a diffusion coefficient D of $4.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was calculated from I_1 by using an electrode of known area.⁴

(26) This outcome provides an a posteriori indication that the ohmic drop correction was properly adjusted in the digital acquisition of the experimental curves. It is well-known that improper ohmic-drop compensation leads to both a negative shift and a broadening of the voltammetric curves; in terms of the convolution output this would result in a poor overlapping of the $\log k(E) - E$ plots obtained in the same potential range at different scan rates.

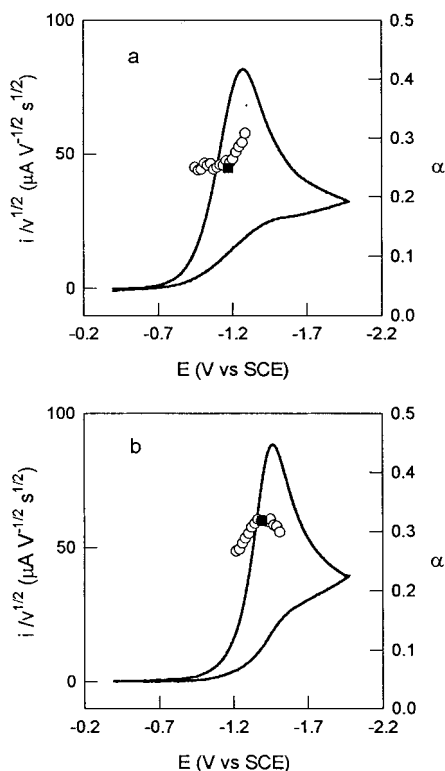


Figure 5. Background-subtracted cyclic voltammograms for the reduction of 1.47 mM CP in DMF/0.1 M TBAP at the glassy carbon electrode, $T = 25\text{ }^{\circ}\text{C}$. The curves were obtained at (a) 0.2 V s^{-1} and (b) 20 V s^{-1} . Also reported in the graphs are the convolution α data (○) and the peak-width α datum (■).

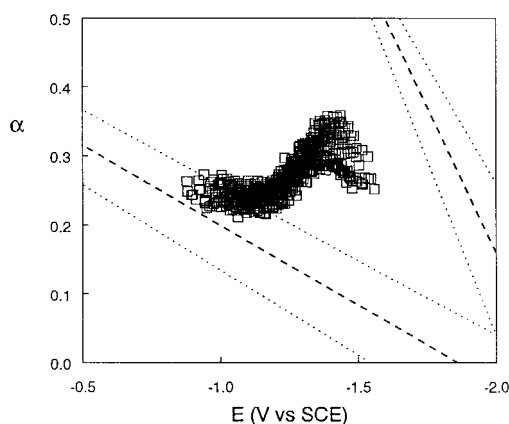


Figure 6. Potential dependence of the transfer coefficient α for the reduction of CP in DMF/0.1 M TBAP at the glassy carbon electrode, $T = 25\text{ }^{\circ}\text{C}$. The data pertain to experiments carried out at scan rates in the $0.1\text{--}50\text{ V s}^{-1}$ range and substrate concentrations in the $1.4\text{--}2.8\text{ mM}$ range. The left and right dashed lines correspond to the behavior expected for the concerted and the stepwise mechanisms, respectively; the dotted lines represent the corresponding uncertainties.

value calculated from the peak width and reported against the mid-potential of the range pertaining to the peak width. The sharpening of the peak on going from 0.2 to 20 V s^{-1} is also worth noting. The result of the α analysis carried out over the whole series of data is plotted in Figure 6, definitely showing that the electrode process is not ruled by a simple ET mechanism; the plot is in fact characterized by a maximum at ca. -1.38 V , corresponding to an average α value of 0.32 . Although not evidenced in Figure 6, which is composed by ca. 600α values, it is worth noting that the same maximum was obtained within only 20 mV at any of the scan rates capable of providing α data in the appropriate potential range (i.e., starting

from ca. 2 V s^{-1}). This means that the observed behavior reflects a real potential dependence of α , beyond experimental error or artifacts.

Such a nonlinear behavior can be explained by hypothesizing that the electrode mechanism changes as a function of the potential. To test this hypothesis, some simple calculations can be performed to check whether the experimental α trend of Figure 6 is in agreement with that expected for a concerted-to-stepwise transition upon decreasing E . Since the theoretical analyses^{3,5} pertaining to ET 1 and ET 3 result in the same quadratic activation-driving force relationship (eq 5), the corresponding transfer coefficients α_n (eq 9) have the potential dependence shown in eq 10. Provided that the ET mechanism

$$\alpha_n = \frac{\partial(\Delta G^\ddagger)_n}{\partial(\Delta G^\circ)_n} = \frac{\partial(\Delta G^\ddagger)_n}{F\partial E} \quad (9)$$

$$\frac{\partial\alpha_n}{\partial E} = \frac{F}{8(\Delta G_0^\ddagger)_n} \quad (10)$$

does not change with the potential, $\partial\alpha/\partial E$ is constant within the approximation for the double-layer effect. As mentioned in the Introduction, $(\Delta G_0^\ddagger)_1$ and $(\Delta G_0^\ddagger)_3$ are given by $\lambda/4$ and $(\lambda + \text{BDE})/4$, respectively. On the basis of the results obtained very recently with other peroxides,⁴ a likely estimate of the heterogeneous reorganization energy λ can be bracketed between the Marcus value and the λ that can be calculated by using an empirical correlation deriving from data pertaining to the reduction of aromatic compounds.²⁷ For both calculations, an effective radius for CP was calculated from the diffusion coefficients of CP (obtained by convolution) and ArCOO^- (through the i_p values for its reduction), using the Stokes-Einstein equation and $r = r_B(2r_{\text{AB}} - r_B)/r_{\text{AB}}$, where r_{AB} and r_B are the radii of CP and ArCOO^- , respectively.^{3,4} Concerning the BDE, we used the value of $36.0 \pm 0.7\text{ kcal/mol}$, which derives from thermolysis data.^{15b} Accordingly, $(\Delta G_0^\ddagger)_1 = 3.4 \pm 0.6$ and $(\Delta G_0^\ddagger)_3 = 12.4 \pm 0.8\text{ kcal/mol}$.

The E° values of ET 1 and ET 3 are also required to complete the picture. Whereas, due to the strong delocalizing properties of the ArCO moiety, the E° for the formation of the radical anion of CP can be safely taken as to be equal within $\sim 50\text{ mV}$ to that of CB (-1.60 V), the E° of the dissociative ET can be calculated through eq 4. The estimation of $E^\circ_{\text{ArCOO}^*/\text{ArCOO}^-}$ is not straightforward but can be carried out in an approximate way by studying the oxidation peak of ArCOO^- , which can be conveniently generated in the DMF solution by reaction of *p*-cyanobenzoic acid with tetrabutylammonium hydroxide. The scan rate dependence indicates that such an oxidation peak is controlled by slow ET kinetics at low to high scan rates, although at a very low scan rate the process falls under mixed kinetic control with a following chemical reaction, most likely H-atom abstraction from DMF by the ensuing aryloxy radical.²⁸ Taking into account reasonable potential shifts from the reversible value, we arrived to the prudential estimate $E^\circ_{\text{ArCOO}^*/\text{ArCOO}^-} = 1.69 \pm 0.1\text{ V}$.^{29,30} Finally, from the reported activation parameters,^{15b} the BDFE of CP can be calculated to be 32.2 kcal/mol . Although the reported error on the activation

(27) The solvent reorganization energy can be calculated by using the Marcus approach and thus by equation $\lambda = e^2(\epsilon_{\text{op}}^{-1} - \epsilon_s^{-1})/4r$, where e is the charge of the exchanged electron, ϵ_{op} and ϵ_s are the high frequency and static dielectric constants of the solvent, respectively, and r is the molecular radius: Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. The correlation, $\lambda(\text{kcal/mol}) = 55.7/r(\text{\AA})$, is obtained using selected values from previously reported data: Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

enthalpy is 0.7 kcal/mol, the error on the free energy is believed to be larger owing to the entropy change, with a much less polar solvent than DMF used in the thermolysis study;^{15b} a more reasonable error is likely within ± 2 kcal/mol. On these grounds, the E° of the dissociative ET is calculated to be 0.29 ± 0.18 V. Although the error on this E° value is much larger than that expected for the formation of CP radical anion, we can nevertheless conclude that the dissociative ET is thermodynamically favored over the stepwise ET by a free energy difference of no less than 1.7 eV.

In the hypothesis that the above barriers and corresponding E° values represent satisfactorily the two limiting situations, it is now possible to estimate the potential dependence of α for both the concerted and the stepwise reduction of CP; the predicted patterns are shown by the dashed lines in Figure 6, the dotted lines accounting for the errors on both the slopes and E° values. In spite of the roughness of the calculations,

(28) That the main reaction underwent by the (4-cyanobenzoyl)oxyl radical is most likely H-atom abstraction from DMF is suggested, for example, by the flash photolysis experiments carried out with di-*p*-methoxybenzoyl peroxide (Maran, F.; Wayner, D. D. M., Unpublished results) that led to the observation that the lifetime of the (4-methoxybenzoyl)oxyl radical decreases by ca. 1.8 orders of magnitude on going from MeCN to DMF, where it reaches the value of 69 ns; by taking into account the possible substituent effects on the lifetime of aroyloxy radicals (Chateaneuf, J.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886), the lifetime of the (4-cyanobenzoyl)oxyl radical is not expected to be significantly different from the above value.

(29) Concerning the voltammetric analysis, we found that the $\partial E_p/\partial \log \nu$ value for the oxidation of ArCOO⁻ is about 45–50 mV/decade at the slowest scan rates, although it increases to about 60 mV/decade when $\nu = 2-5$ V s⁻¹. The calculation of the standard potential was carried out by both classical methods^{13b} and by using the DigiSim software. Whereas a rate constant of 1×10^7 s⁻¹ was assumed for the decay of the radical,²⁸ the heterogeneous standard rate constant was bracketed in the 0.1–0.2 cm s⁻¹ range to fit the experimental peak potentials well within the experimental error. It is relevant to note that, due to the kinetic zone in which the experimental system is,^{13b} even by allowing the chemical rate constant to be in error by as much as 1 order of magnitude, the uncertainty in the standard potential is within 50 mV. A larger error, however, was prudently assumed due to the problems associated to voltammetric measurements in DMF at such positive potentials.

(30) It should be added that we arrived in a similar way to 1.5 V as a preliminary estimate of the standard potential of the corresponding PhCOO⁻/PhCOO[•] couple,¹⁸ in reasonable agreement with a recent, nonelectrochemical estimate of it, 1.24 V: Andrieux, C. P.; Savéant, J.-M.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1996**, *118*, 9788.

the experimental α data indeed seem to tend to such lines, therefore supporting the hypothesis of a concerted-to-stepwise mechanism transition caused by the different sensitivity of $(\Delta G^\ddagger)_1$ and $(\Delta G^\ddagger)_3$ to changes in the driving force. The reduction of CP seems to proceed mostly through a concerted mechanism as long as E is more positive than $E^\circ_{\text{ArCOO}^-/\text{ArCOO}^\bullet}$ by ~ 0.7 V. On the other hand, when E is changed to more negative values, the rate of the stepwise process starts becoming more competitive to the concerted, one-step process. Although a complete transition was not observed in the potential range in which the α data could be collected (due to the experimental limitations), the α pattern of Figure 6 seems to provide a well-behaved case of a borderline ET bond fragmentation mechanism, beyond the experimental error. It is also worth noting the result shown in Figure 5: since the α values that can be collected for each ν value span a typical E range of 0.3–0.35 V, the convolution analysis allowed us to detect a partial mechanism transition even within a single voltammetric curve, a possibility that is obviously precluded when only one average α value per curve is determined by the conventional voltammetry approach.

The reduction of CP thus provides another convincing support to the Savéant theory of dissociative electron transfer³ and relative implications. Considering the state of the art for research on dissociative ETs, at least one final observation should be made: since one of the most important requirements to detect a borderline ET bond fragmentation mechanism is the difference between the standard potentials of ET 1 and ET 3, one might also expect that within families of related compounds (similar BDE and λ values) experimental outcomes analogous to that of CP should be observed once the difference $E^\circ_{\text{AB}/\text{A}^\bullet, \text{B}^-} - E^\circ_{\text{AB}/\text{AB}^\bullet}$ is kept to similar values by proper selection of the ring substituent. Further studies are currently underway in our laboratory to verify this expectation.

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